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(54) UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR PUITS DE FORAGE (54) USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING

FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environment- ally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

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(54) Titre: UTILISATION DE COMPOSES TENSIO-ACTIFS A BASE DE GLYCOSIDE ALKYLE DANS DES FLUIDES DE FORAGE A BASE D'EAU ET D'HUILE ET AUTRES AGENTS DE TRAITEMENT POUR PUITS DE FORAGE (54) Title: USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

(57) Abrégé/Abstract:

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and OW type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits. The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.



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Abstract of the Disclosure

Described is the use of surface-active alkyl glycoside compounds as ecologically compatible emulsifiers of the W/O type and O/W type, respectively, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits.

The invention further relates to inverted drilling fluids which are suitable for a non-polluting exploitation of geological resources and contain a continuous oil phase and, present therein, a dispersed aqueous phase together with emulsifiers, further conventional auxiliary agents such as thickeners, fluid-loss additives, weighting agents, water-soluble salts and/or alkali reserves, said inverted drilling fluids being characterized in that they contain surface-active alkyl glycoside compounds of formula (I) as emulsifier or as an emulsifier component together with an ecologically compatible continuous oil phase.

USE OF SURFACE-ACTIVE ALKYL GLYCOSIDE COMPOUNDS IN WATER- AND OIL-BASED DRILLING FLUIDS AND OTHER DRILL-HOLE TREATMENT AGENTS

The invention relates to the use emulsifiers having an increased ecological compatibility for the production of fluid dispersed systems which are present either as W/O inverted emulsions comprising a continuous oil phase or as aqueous emulsions containing a dispersed oil phase and which are suitable for the technical application within the field of use of fluid drill-hole treatment agents. Referring to a characteristic example for agents of this kind, the invention is described hereinbelow by way of oil-based and waterbased drilling fluids, respectively, and drilling muds formed therewith. However, the field of application of the modification according to the invention of auxiliary liquids of the kind involved here is not limited thereto, while it also includes in particular the areas of spotting fluids, spacers, auxiliary liquids for workover and stimulation and for fracturing.

More particularly, the invention substantially influences the ecological compatibility of said auxiliary agents which are being worldwide used today by employing selected and, more specifically,

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ecologically acceptable types of emulsifiers. In its preferred embodiment the invention intends to use said biologically acceptable emulsifiers simultaneously in combination with oil phases having an increased environmental compatibility and especially a biological degradability.

In the area of liquid sweeping systems for rock-drilling to bring-up the removed drill cuttings, the so-called inverted drilling muds are of excellent importance which, based on W/O emulsions, contain a dispersed aqueous phase in the continuous phase. The content of the dispersed aqueous phase usually is within the range of from about 5 to 50% by weight.

However, also known are water-based drilling fluids comprising an emulsified dispersed oil phase (O/W type), the oil content of which may range from some percent to about 50% by weight. O/W emulsion fluids of this kind exhibit a number of considerable advantages over merely water-based fluid systems.

The stabilization of each of the selected dispersion forms requires the use of appropriate emulsifiers either of the W/O type (inverted fluids) or of the O/W type (emulsion fluids), respectively. Hereto, reference is made to the pertinent literature, for example, G. R. Gray, H. C. H. Darley, "Composition and Properties of Oil Well Drilling Fluids", 4th Edition, Gulf Publishing Cp., Houston, London 1981, especially pages 51, 64 and 320 et seq..

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Today the oil phases of drilling fluids of the type described here and comparably composed other drill-hole treatment agents in practice are almost exclusively formed by mineral oil fractions. This involves a considerable environmental pollution, if, for example, the drilling muds directly or via the drilled rock will Mineral oils are only . infiltrate the environment. difficult to decompose and are virtually not anerobically degradable at all and, thus, to be rated as longterm pollutants. Nevertheless, even if these oil phases as the main constituent or at least a substantial portion of the drilling fluid make a significant starting point for ecological considerations, an equivalent attention will have to be paid also to the other components of such multi-component systems. Here, the emulsifiers are of specific importance. Compounds of this type, in accordance with the intended use thereof, are highly active substances already at a low concentration which are known to be capable of an intense interaction with the vegetable or animal organism.

Summary of the Invention

The present invention substantially improves the working agents of the described type based on continuous or dispersed oil phases in appreciation phases, in aqueous admixture with of the ecological compatability thereof, over working agents of this kind as common to-day. the invention, for the specifically, emulsifiers provides field of use as involved here, and/or emulsifier combinations which have been per se known and have been described to be environmentally compatible to a high degree, while they have not been put into use in the field of use involved here. preferred

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embodiment of the invention, these environmentally compatible emulsifiers of the W/O type or of the O/W type are to be employed in combination with oil/water phases, where the oil phases themselves have an increased ecological compatibility and, more specifically, are capable of being decomposed by natural degradation mechanisms doing little harm to the environment.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The invention provides the use of <u>per se</u> known surface-active alkyl glycoside compounds ecologically compatible or acceptable compounds which, depending on their constitution and kind of interaction with the surrounding system are to be classified as W/O

emulsifiers or as O/W emulsifiers.

Thus, in a first embodiment, the invention relates to the use of surface-active alkyl glycoside compounds of the W/O type and/or O/W type, as ecologically compatible emulsifiers, in fluid and pumpable drilling fluids and other fluid drilling-hole treatment agents which comprise a continuous or a dispersed oil phase together with an aqueous phase and which are suitable for an environmentally acceptable exploitation of geological resources, for example oil or natural gas deposits.

of particular importance in this context are the corresponding inverted drilling fluids which in a continuous oil phase contain a dispersed aqueous phase together with emulsifiers and further conventional auxiliary agents such as thickeners, fluid-loss

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additives, weighting agents, soluble salts and/or alkali reserve. In this embodiment according to the invention there is provided the use of surface-active alkyl glycoside compounds of the W/O type as emulsifier or at least as a component of an ecologically compatible emulsifier system.

Preferred is the use of emulsifiers based on surface-active alkyl glycoside compounds in combination with environmentally compatible ester oils, oleophilic alcohols and/or corresponding ethers as continuous or dispersed oil phase. Here particular reference is to be made to pertinent developments by applicant describing, in a greater number older patent applications, proposals for substituting the previously common mineral oil fractions with ecologically compatible readily degradable oil phases. Thereby, various types of substituting oils have been presented which may also be used as They include selected oleophilic monocarboxylic acid esters, selected polycarboxylic acid esters, at least largely water-insoluble alcohols which are fluid under the operation conditions, corresponding ethers and selected carbonic acid esters. reference is made here to the older Canadian Patent Applications Nos. 2,006,010; 2,006,009;

2,047,697; 2,047,706; 2,009,689; 2,009,688; 2,051,624; 2,050,935; 2,084,780; and 2,085,610.

All of the older

applications mentioned here relate to the field of oil-based drilling fluid systems, especially of the W/O inverted type. Water-based emulsion fluids using these oil phases of an increased degradability have been described in the older Canadian applications

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2,058,636; 2,057,005; 2,057,061; 2,084,780; and 2,085,610 as already mentioned.

The invention, in its most important embodiment, comprises the use, in combination, of the above-described emulsifiers of the class of the surface-active alkyl glycoside compounds together with dispersed or continuous oil phases of the type described last.

Detailed Description of the Invention

Surface-active alkyl glycoside compounds and the preparation thereof have been described in detail in the state of prior art, while emphasis so far has been laid on the use thereof as O/W emulsifiers - for example in the context of detergents and cleansers. In this context, reference is made to the DE-Al 38 33 780 and the primary literature quoted therein. A more recent proposal - cf. hereto the DE-Al 37 20 330 - provides the use, in combination, of alkyl glycosides within the scope of the so-called tertiary recovery of crude oil from appropriate deposits.

The alkyl glycoside compounds - as above - which are now to be used for the intended use according to the invention may be characterized by the following formula (I)

 $R-O-Z_{D} \tag{I}$

wherein

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R in said formula represents linear and/or branched alkyl which may be saturated and/or olefinically unsaturated and has at least 7 carbon atoms in the moiety R. Preferred are corresponding moieties R having from 8 to 22 carbon atoms.

Z represents one or more moieties of aldoses and/or ketoses, among which here especially the hexose and/or pentose moieties are to be considered.

n characterizes the random oligomer distribution of the moieties Z. Numerically n represents a number of from 1 to 10 on the average, preferably of from 1.1 to about 5. Of particular importance are alkyl glycoside compounds having the general formula (I) wherein the numerical value of n is within the range of from about 1.2 to 2.5.

The term surface active alkyl glycoside compounds as used according to the invention is meant also to include the corresponding reaction products of sugars and monofunctional alcohols. As the sugar components in the widest sense there are to be contemplated the aldoses and ketoses designated as glycoses. There may be mentioned glucose, fructose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and ribose. For the preparation of the alkyl glycoside compounds aldoses are preferred to be used because of their higher reactivity, Among the aldose special importance is attributed to glucose due to its easy accessability and availablity in commercial amounts.

The monofunctional alcohols employed for the acetalization, more particularly, are the surfactant

alcohols having from 8 to 22 carbon atoms as commercially available on a large scale, among which native and/or Native alcohols are synthetic alcohols are usable. known to be obtained from the hydrogenation of fatty acids and fatty acid derivatives. Typical synthetic components are the known oxoalcohols and/or Ziegler alcohols. The alcohols themselves may be saturated, but they may be olefinically unsaturated as well. chain alcohols are of particular importance because they are quickly and trouble-free degradable. also branched alcohols, for example those of the kind of the oxoalcohols, are to be considered as ecologically compatible components and are suitable for acetalizing to form the alkyl glycoside compounds of the type used in the invention.

Alkyl glycoside compounds are excellent emulsifier components within the scope of the invention not only because of their biologic acceptability, but they are known to exhibit considerable alkali stability in the form of acetals. Drilling-hole treatment agents of the kind involved here, and especially drilling fluids, as a rule are composed such as to include alkali reserves, for example in order to be capable of counteracting the invasion of acidic reactants from the drilled rock. Said alkali stability of the alkyl glycoside compounds is an essential feature of the suitability thereof in practical use. At the same time they provide - depending on their specific structures - highly stable W/O emulsions.

The classification of the emulsifiers in each of the classes mentioned above is in a <u>per se</u> known manner governed by the ratio of the oleophilic portions



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in a given molecule to the hydrophilic portions of said molecule. The assignment may be achieved by way of the so-called HLB value; thereby the typical W/O emulsifiers are known to be characterized by comparably low HLB values - such as those within the range of from 3 to 11 or 12 - whereas the classical O/W emulsifier will occupy the higher range of the numerical HLB values. Also in the field as here concerned of the drilling hole treatment agents the above classification is made use of; cf. hereto, e.g., the literature reference Gray, Darley loc. cit., page 321, as quoted above.

The preferred functionability of each of selected alkyl glycoside compounds having the general formula (I) is derived from its structural members. The oleophilic molecule portion is coined by the moiety R of said formula. The sugar moiety Z, and here especially the oligomer distribution thereof — represented by the random numerical value for n — will form the hydrophilic molecule portion. Accordingly, W/O emulsifiers of this kind are characterized by having markedly oleophilic molecule portions with a restriction of the hydrophilic molecule portion, while the reversed situation is applicable to the case of the typical O/W emulsifiers.

Accordingly, for the stabilizing of W/O emulsions there are particularly suitable those compounds of the general formula (I) which at least partially, and preferably to a prevailing extent, comprise moieties R having 10 and more carbon atoms, and preferably at least 12 carbon atoms. Alcohol moieties of this kind comprising 16 to 18 carbon atoms may be of particular importance for technical as well as economical reasons. At the same time here the random mean value n for the

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glucose moiety as usually present is restricted to values below about 2.5 and preferably to maximum values of about 2. In preferred embodiments n may be within the range of from about 1.2 to 1.8.

Typical O/W emulsifiers, on the other hand, are the alkyl glycoside compounds as described in the quoted DE-Al 38 33 780 for washing and cleaning agents, which alkyl glycoside compounds are derived, for example, from Here the numerical value of n may C₁₀₋₁₄-alcohols. reach higher values within the range as indicated. Howewer, it has been known that among the alkyl glycosides based on these comparably lower alcohols having about 8 to 14 carbon atoms highly active O/W emulsifiers are obtained also in the case that numerical value of n is, for example, within the range of from about 1.2 to 1.5. It is one characteristic feature with respect to the use of the alkyl glycoside compounds within the teaching of the invention that relatively easy shifts molecular structure may influence the suitablity of the respective component(s) while, however, it is likewise a characteristic feature that among the compounds which are interesting under a preparation-technological aspect there is a relative large group of compounds suitable as stabilizing emulsifiers of the W/O type as well as of the O/W type. Here the type of emulsion formed is to a high degree co-determined by the total composition of the particularly involved drilling fluid or the corresponding drilling mud.

The alkyl glycoside-based emulsifiers, in a preferred embodiment, are employed as the essential components forming the type of emulsion and stabilizing the emulsion. Nevertheless the teaching according to the - 111 -

invention also includes mixed systems in which alkyl glycosides are used together with other emulsifier components. It is preferred that these other emulsifier components on their own are ecologically compatible; in this context reference may be made to applicant's older Canadian Patent Application No. 2,075,208

wherein selected ether-based and di-salt-based emulsifiers, respectively, for oil-based inverted emulsions have been described.

If such emulsifier mixtures are used, then in preferred embodiments of the invention the alkyl glycoside compounds constitute at least 10% by weight, and preferably at least 50% by weight, of the respective emulsifier system.

The alkyl glycoside compounds may be used in amounts of from about 0.1 to 10% by weight, relative to the sum of the liquid phases water and oil. Preferred amounts are within the range of from about 0.5 to 5% by weight of the emulsifier components, while the range of from about 1 to 3% by weight of the emulsifier - again relative to the sum of water + oil - is of particular importance.

Within the scope of the so far known preparation of surface-active alkyl glycoside compounds it is desired that the alcohol employed in an excessive amount in the acetalization reaction is separated from the product of the acetalization to such an extent that at best a few percent of free alcohol would remain in the reaction mixture. Reference is made to the corresponding information set forth in the DE-Al 38 33 780 and the

method described therein to attain said purpose by thin film evaporation for recovering the alcohol. Operating in accordance with the invention will not require said The alcohols R-OH comparably expensive process step. employed for the acetalization throughout are oleophilic alcohol components which are present in an excessive amount and in admixture with the alkyl-glycoside formed or may be supplied to the intended use. If desired, the excess amount of alcohol may be partially removed while, however, in a preferred embodiment of the invention it is provided to employ the alkyl glycosides together with at least about 50% by mole and preferably together with about 100% by mole of free alcohol - % by mole in each case relative to alkyl glycoside compound. economical production of the emulsifiers according to the invention is further facilitated by omitting the step of bleaching the reaction products as primarily obtained, which step in prior art as evidenced by the pertinent printed publications is considered as an essential process step. Thus, the production process substances containing compositions of active alkyl glycoside compounds within the scope of the invention may be restricted to the process step of acetalization - expediently in the presence of acidic The crude reaction product may be directly catalyst. put into a commercial use.

As to the forms of the alkyl glycosides for handling in practice, two essentially anhydrous formulations have proven to be useful: For one, the alkyl glycosides may be stored and handled as concentrated solutions in preferably ecologically acceptable oil phases. On the other hand, it is possible to employ the alkyl glycosides as solids - here especially as granules. Since the D 9223

emulsifier compounds as such, although they are usually solids, tend to sticking and/or smearing, it may be appropriate to additionally use particulate solids in the formation of the respective granules. Here typical auxiliary materials used in crude oil technology and particulate in nature are suitable, for example weighting agents, salts, viscosity builders and the like, or inert auxiliary materials may be included in the use.

In the preferred embodiment as especially featured in the introduction, the appropriate oil phases are constituted by the ecologically compatible ester oils, oleophilic alcohols and/or ethers described in applicant's older applications as quoted. When said agents are used, the invention relates to the drill-hole treatment agents which are fluid and pumpable within the temperature range of from 5 °C to 20 °C, and more specifically drilling fluids based on

- either a continuous oil phase, especially in admixture with a dispersed aqueous phase (W/O inverted type)
- or a dispersed oil phase in a continuous aqueous phase (O/W emulsion type).

The ecologically compatible oils and oil phases, with respect to the possible physical properties thereof, cover a wide range. The invention comprises, on the one hand, oil phases which are fluid and pumpable also at low temperatures. These, more particularly, include representatives suitable for the preparation of W/O emulsions. However, on the other hand, highly viscous to solid oil phases and materials of this type may also be included in the use within the scope of the teaching according to the invention. This may be exemplified by the following deliberations:

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For water-based O/W emulsion fluids a high mobility of the dispersed oil phase is not required and, as the case may be, not even desirable. For example, to ensure good lubricating properties, oil phases adjusted such as to be comparably viscous may be advantageous. Another possible use of highly viscous or even solid ecologically compatible oil phases may be constituted, if the respective oil phase involved in the final product is only partially formed by said highly viscous to solid representatives of degradable esters, alcohols and/or ethers which themselves have been admixed with comparably highly liquid oils of this kind.

Nevertheless, there is consistently applicable to all oil phases or mixed oil phases to be used according to the invention that flash points of at least about 100 °C and preferably flash points of above about 135 °C are demanded for reasons of safety in operations. Values that are distinctly higher, particularly those above 150 °C, may be especially expedient. Furthermore, there is consistently applicable to the oil phases as potentially susceptible to hydrolysis that may be used within the scope of the invention not only that the requirement of the ecological compatibility will have to be met by the compound put into use, i.e., for example, the respectively selected ester oil or ester oil mixture, but also that no toxicological and especially no inhalation-toxicological danger will be induced upon a partial saponification in practical use. Within the scope of the mentioned older applications there has been described in great detail that here, more particularly, the various representatives of ester oils are referred to, with the monofunctional alcohols from the esters formed being again of particular significance here.

comparison to polyfunctional alcohols, the lower members of the monofunctional alcohols are highly volatile, so that here a partial hydrolysis may cause exposure to secondary danger. Accordingly, in the classes of the various ester oils those monofunctional alcohols included in the use, or the moieties of such alcohols, have been chosen so that they have at least 6 carbon atoms, and preferably at least 8 carbon atoms, in the molecule thereof.

The inverted drilling fluids of the kind involved according to the invention, irrespectively of a definite property of the continuous oil phase, in preferred embodiments have a plastic viscosity (PV) within the range of from 10 to 60 mPa.s and a flow limit (yield point, YP) within the range of from 5 to 40 lb/100 ft² - each determined at 50 °C.

As an oil phase which is ecologically compatible and well fluid at low temperature, there have proven to be useful, more specifically, ester oils of monocarboxylic acids which then, in a preferred embodiment of the invention, are derived from at least one of the following subclasses:

- a) Esters of C₁₋₅-monocarboxylic acids and monoand/or polyfunctional alcohols, whereof the moieties of monohydric alcohols comprise at least 6 carbon atoms and preferably at least 8 carbon atoms and the polyhydric alcohols preferably have from 2 to 6 carbon atoms in the molecule,
- b) Esters of monocarboxylic acids of synthetic and/or natural origin comprising from 6 to 16 carbon

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atoms, and more specifically esters of aliphatic saturated monocarboxylic acids and mono- and/or polyfunctional alcohols of the kind mentioned in a),

c) Esters of olefinically mono- and/or polyunsaturated monocarboxylic acids having at least 16, and especially 16 to 24 carbon atoms and especially monofunctional straight-chain and/or branched alcohols.

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Starting materials for recovering numerous monofalling under these subclasses, carboxylic acids especially those having a higher number of carbon atoms, are vegetable and/or animal oils. There may be mentioned coconut oil, palm kernel oil and/or babassu oil, especially as feedstock for the recovery of monocarboxylic acids of the prevailing range up to C, and of Ester oils essentially saturated components. vegetable origin based on olefinically mono- and optionally poly-unsaturated carboxylic acids of the range of C₁₆₋₂₄ are, for example, palm kernel oil, peanut oil, castor oil, sunflower oil, and especially rapeseed oil. But also components synthetically recovered are important structural elements for ecologically compatible oil phases on the side of the carboxylic acids as well as on the side of the alcohols.



Preferably, the oil phase has a solidification of below about 0°C and a Brookfield Viscosity at zero to 5°C of less than about 55 mPa.s.

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Additives to the oil-based and/or water-based fluid

Inverted drilling muds conventionally contain, together with the continuous oil phase, the finely dispersed aqueous phase in amounts of from 5 to 50% by weight. In water-based emulsion fluids the dispersed

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oil phase is usually present in amounts of from at least about 1 to 2% by weight, frequently in amounts of from at least about 5% by weight with an upper limit of the oil portion of about from 40 to 50% by weight — the percentage by weight in all cases being based on the sum of the unloaded liquid portions of oil/water.

Besides the water content, there are to be taken into consideration all of the additives provided for comparable types of fluids. Said additives may be water-soluble, oil-soluble and/or water-dispersible and/or oil-dispersible.

Conventional additives, besides the emulsifiers the invention, include, defined according to example, fluid-loss additives, soluble and/or insoluble materials to build-up structural viscosity, alkali reserve, agents for inhibiting an undesirable water exchange between drilled formations - e.g. water-swellable clays and/or salt layers - and the, e.g., waterbased drilling fluid, wetting agents for an improved strike of the emulsified oil phase on solid surfaces, e.g. for improving the lubricating effect, but also for improving the oleophilic closure of exposed rock formations, e.g. rock surfaces, biocides, for example for inhibiting bacterial onset and growth of emulsions and the like. In detail, reference is here to be made to pertinent prior art such as described, for example, in the technical literature as initially quoted; cf., more specifically, Gray and Darley, loc. cit., Chapter 11, "Drilling Fluid Components". way of an excerpt, there may be quoted:

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Finely dispersed additives for increasing the density of the fluid: Widely used is barium sulfate (baryte), but also calcium carbonate (calcite) or the mixed carbonate of calcium and magnesium (dolomite) are used.

Agents for a build-up of structural viscosity which simultaneously will act as fluid-loss additives: Here, bentonite of hydrophobized bentonite are to be mentioned in the first place. For salt water fluids, other comparable clays, and more specifically attapulgite and sepiolite are of considerable importance in practice.

Also the use in combination of organic polymer compounds of natural and/or synthetic origin may be of considerable importance in this connection. There may be especially mentioned starch or chemically modified starches, cellulose derivatives such as carboxymethylcellulose, guar gum, xanthan gum, or also merely synthetic water-soluble and/or water-dispersible polymer compounds, especially of the type of the high molecular weight polyacryl amide components with or without anionic or cation modifications, respectively.

Diluents for regulating the viscosity: The socalled diluents (thinners) may be organic or inorganic in nature. Examples for organic thinners are tannin and/or quebracho extract. Further examples are lignite and lignite derivatives, especially lignosulfonates. However, as has been set forth hereinabove, in a preferred embodiment, just here no toxic compounds will be included in the use, among which in the first place the respective salts with toxic heavy metals such as chromium and copper are to be mentioned. Polyphosphate D 9223

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compounds constitute an example of inorganic thinners.

Additives inhibiting the undesirable water-exchange with, for example, clays: Here to be considered are the additives known from prior art for oil- and water-based drilling fluids. These include halides and/or carbonates of the alkali and/or alkaline earth metals, whereof the potassium salts, optionally in combination with lime, may be of particular importance.

Reference may be made, for example, to the relevant publications in "Petroleum Engineer International", September 1987, 32-40, and "World Oil", November 1983, 93-97.

Alkali reserves: Here to be taken into consideration are inorganic and/or organic bases adjusted to match the total behavior of the fluid, and more particularly basic salts or hydroxides of alkali and/or alkaline earth metals as well as organic bases. Kind and amount of these basic components will have been selected and mutually adjusted in a known manner so that the drilling hole treating agents will be adjusted to a pH value within the range of from about neutral to moderately basic, especially to the range of from about 7.5 to 11.

Basically, the amounts of each of the auxiliary materials and additives is within the conventional range and, thus, may be learnt from the relevant literature as quoted.

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EXAMPLES

In the following Examples 1 to 4, by observation of a standard formulation for oil-based drilling fluid systems of the W/O type there are set forth appropriate drilling fluid systems, wherein each continuous oil phase is formed by a selected oleophilic carboxylic acid ester of the following definition:

An ester mixture comprising substantially saturated fatty acids based on palm kernel and 2-ethylhexanol which to the by far predominating part is derived from $C_{12/14}$ -carboxylic acids and conforms to the following specification:

 C_8 : from 3.5 to 4.5% by weight C_{10} : from 3.5 to 4.5% by weight C_{12} : from 65 to 70 % by weight

 c_{14}^{--} : from 20 to 24 % by weight

C₁₆: about 2 % by weight

c₁₈: from 0.3 to 1 % by weight

The ester mixture is a bright yellow liquid which has a flash point in excess of 165 °C and a viscosity (Brookfield, 20 °C) of from 7 to 9 cP.

The viscosity characteristics are determined with unaged and aged material as follows:

Measurement of the viscosity at 50 °C in a Fann-35-viscosimeter from the company Baroid Drilling Fluids, Inc.. In a <u>per se</u> known manner there have been determined the plastic viscosity (PV), the yield point (YP) and the gel strength (lb/100 ft²) after 10 seconds and after 10 minutes. In Example 1 there is further determined the fluid loss value (HTHP).

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Ageing of the respective drilling fluid is effected by way of a treatment at 125 °C in an autoclave - in a so-called roller oven - for 16 hours.

The drilling fluid systems are composed in a per se known manner in accordance with the following basic formulation:

- 230 ml of carboxylic acid ester oil
 - 26 ml of water
 - 6 g of organophilic bentonite (GELTONE from the company Baroid Drilling Fluids,
 Inc.)
 - g of organophilic lignite (DURATONE from the company Baroid Drilling Fluids, Inc.)
 - 2 g of lime
 - 6 g of emulsifier based on alkyl glycoside
 - 3 g of co-emulsifier based on C₁₈ fatty acid
 only used in Examples 3 and 4 -
- 346 g of baryte
 - '9.2 g of CaCl₂ . 2 H₂O

Example 1

As an emulsifier based on alkyl glycoside there is employed the condensation product of glucose and C_{16} -fatty alcohol of natural origin (commercial product "Lorol C_{16} " of applicant). The characteristic values - as indicated above - determined of the unaged and of the aged materials have been compiled in the following summarizing Table.

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	• • •	
•	Unaged Material	Aged Material
Plastic viscosity (PV)	41	44
Yield point (YP) Gel strength (lb/100 ft ²)	14	22
10 seconds	7	18
10 minutes	11	36

HTHP 3 ml

Example 2

In this Example there is employed, as an emulsifier based on alkyl glycoside, the reaction product of glucose with a fatty alcohol mixture of natural origin with a by far prevailing chain length of C_{12-14} (commercial product "Lorol 1214" of applicant). The characteristic values determined of the unaged and of the aged materials are as follows:

	Unaged Material	Aged Material
Plastic viscosity (PV)	41	42
Yield point (YP)	15	18
Gel strength (lb/100 ft ²)		
10 seconds	8	13
10 minutes	11	25

HTHP 5 ml

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Example 3

The run of Example 1 is repeated, except that - as initially indicated - a co-emulsifier based on C₁₈-fatty acid is additionally employed. The characteristic values determined of the unaged and of the aged materials are as follows:

	Unaged Material	Aged Material
Plastic viscosity (PV)	37	36
Yield point (YP) Gel strength (lb/100 ft ²)	7	. 8
10 seconds	5	6
10 minutes	11	5

Example 4

The run of Example 2 is repeated, except that also here a co-emulsifier based on C_{18} -fatty acid is additionally employed. The characteristic values determined of the unaged and of the aged materials are as follows:

·	Unaged Material	Aged Material
Plastic viscosity (PV)	38	35
Yield point (YP) Gel strength (lb/100 ft ²)	13	10
10 seconds	7	5
10 minutes	14	9

Example 5

In the following Example 5 a water-based emulsion fluid using a complex oleophilic polycarboxylic acid ester having lubricating properties is prepared as a dispersed oil phase in accordance with the following procedure:

First, a homogenized slurry containing 6% by weight of bentonite is produced from a commercially available bentonite (non-hydrophobized) and tap water and the pH value thereof is adjusted to from 9.2 to 9.3 with caustic soda solution.

This pre-swollen bentonite phase is charged and, in subsequent process steps - each with thorough mixing - , the individual components of the water-based ester-oil emulsion are incorporated in accordance with the following formulation:

- 350 g of 6% by weight bentonite solution.
 - 1.5 g of commercial carboxymethylcellulose (of low viscosity) (Relatin U 300 S 9)
- 35 q of sodium chloride
- 70 g of complex ester
- 3 g of emulsifier of Example 2
- 219 g of baryte

As an oleophilic ester oil phase there is employed the reaction product of trimethylolpropane (14% by weight), a commercially available dimer fatty acid mixture (24% by weight) and oleic acid as the balance. The dimer fatty acid mixture contains 77% by weight of dimer acids and tri- and higher polycarboxylic acids as the balance - here % by weight relative to the dimer fatty acid mixture.

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The viscosity of the O/W emulsion fluid thus prepared is determined as follows:

First the plastic viscosity (PV), the yield point (YP) and the gel strength after 10 seconds and 10 minutes of the unaged emulsion fluid are determined at room temperature.

Then the emulsion fluid is aged under static conditions at 90 °C for 16 hours in order to test the influence of the temperature on the stability of the emulsion. Then the viscosity values are once more determined at room temperature.

	Unaged Material	Aged Material
Plastic viscosity (PV)	. 18	16
Yield point (YP) Gel strength (1b/100 ft ²)	101	114
10 seconds	49	52
10 minutes	50	53

CLAIMS:

- An invert emulsion drilling fluid composition suitable for the environmentally-acceptable development of a geological resource, said composition comprising;
 - (a) an ecologically-compatible continuous oil phase;
 - (b) an aqueous phase dispersed in said oil phase;
 - (c) a thickening agent;
 - (d) a fluid-loss additive;
 - (e) a weighting agent;
 - (f) an alkali reserve component; and
 - (g) a water-in-oil emulsifier component comprising a surface-active alkyl glycoside.
- 2. A composition as in claim 1, wherein said alkyl glycoside has the structural formula I:

$$R - O - Z_n \tag{I}$$

wherein:

- R represents a linear or branched, saturated or unsaturated alkyl radical containing at least 8 carbon atoms;
 - Z represents one or more aldose or ketose units; and
 - n has an average value of 1 to 5.
- 3. A composition as in claim 2, wherein R contains at least 12 carbon atoms and n has a maximum value of 2.
- 4. A composition as in claim 1, 2 or 3, wherein said alkyl glycoside is present in the amount of about 0.1 to about 10% by weight, based on the sum of the weight of said oil phase and said aqueous phase.

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- 5. A composition as in any one of claims 1 to 4, wherein said oil phase is selected from the group consisting of an ester oil of a mono- or polycarboxylic acid and a mono- or polyfunctional alcohol, a carbonic acid ester oil, an oleophilic alcohol and an oleophilic ether.
- 6. A composition as in claim 5, wherein said ester oil of a mono- or polycarboxylic acid and a mono- or polyfunctional alcohol is selected from the group consisting of:
- a) an ester of a C_1 - C_5 monocarboxylic acid and a monoor polyfunctional alcohol wherein said monofunctional alcohol contains at least 6 carbon atoms and said polyfunctional alcohol contains from 2 to 6 carbon atoms in the molecule;
- b) an ester of a C_6 - C_{16} aliphatically saturated monocarboxylic acid and a mono- or polyfunctional alcohol as in a); and
- c) an ester of a mono- or polyolefinically unsaturated $C_{16}-C_{24}$ monocarboxylic acid and a monofunctional straight chain or branched alcohol.
- 7. A composition as in any one of claims 1 to 6, wherein said oil phase has a flash point of at least about 100°C.
- 8. A composition as in any one of claims 1 to 7, wherein said oil phase has a solidification value of below about 0°C and a Brookfield viscosity at 0 to 5°C of less than about 55 mPa.s.
- 9. A composition as in any one of claims 1 to 8, having a plastic viscosity of from about 10 to about 60 mPa.s and a yield point of from about 5 to about 40 lbs/100 ft², each determined at about 50°C.

- 10. A composition as in any one of claims 1 to 9, wherein said aqueous phase comprises from about 5 to about 50% by weight of said composition, and contains CaCl₂ or KCl salts dissolved therein.
- 11. A composition as in any one of claims 1 to 10, wherein said geological resource is an oil or natural gas deposit.
- 12. A process of developing a geological resource by drilling, comprising contacting said resource during drilling with an ecologically-acceptable composition as in any one of claims 1 to 11.

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